A method for predicting hydrogen and oxygen isotope distributions across a region's river network using reach-scale environmental attributes

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Abstract. Stable isotope ratio measurements (isotope values) of surface water provide information on hydrological processes
10   and can be used to determine provenance of hydrogen and oxygen stored in animal and plant tissues. Development of maps of
the distribution of isotope values (isoscapes) for river networks is limited by methods to interpolate point measures to values
for the entire network. Isotope values of precipitation and environmental characteristics that drive fractionation processes
within the catchment also affect downstream reaches via flow. Many environmental characteristics, such as man-made dams,
are no more likely to affect nearby unconnected reaches than distant ones. Hence, distance-based geospatial and statistical
15   interpolation methods used to develop isoscapes for precipitation and terrestrial systems are less appropriate for river networks.
We used a water balance-based method, which represents patterns of surface flow and mixing, and added a regression-based
correction step using catchment environmental predictors. We applied this method across the river network of New Zealand,
comprising over 600,000 reaches and over 400,000 kilometres of rivers. Inputs to the model are national rainfall precipitation
isoscapes, a digital elevation layer, a national river water isotope monitoring dataset (3 years of monthly sampling at 58 sites)
20   and reach scale river environmental databases across the New Zealand river network. δ^2H and $\delta^{18}O$ isoscapes produced using
this regression-based kriging method showed improved fit to validation data, compared to a model for which residuals were
applied as a correction factor across the river network using ordinary kriging. The resulting river water isoscapes have potential
applications in ecology, hydrology and provenance studies for which understanding of spatial variation between precipitation
and surface water isotope values are required.

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1 Introduction

Stable hydrogen and oxygen isotope measurements in surface water provide powerful tools for hydrology, ecology and food science; uses include identifying runoff sources to rivers, quantifying land-atmosphere water fluxes, determining natal origins

30 of migratory fish, and tracing the geographical origins of food (Kelly et al., 2005; Cable et al., 2011; Gao and Beamish, 1999; Gibson et al., 1996). Therefore, it is important to know spatially explicit distributions of hydrogen and oxygen stable isotope ratios (hereafter isotope values, following delta notation (Coplen, 2011)) for water bodies. Isotope values in rivers are strongly dependent on that of precipitation (Kendall and Coplen, 2001), mixing of water sources, and isotopic fractionation resulting from different hydrologic processes occurring at and below the land surface within their catchments. Variations in the isotope

35 values of precipitation reflect the temperature at which condensation occurs and prior condensation as air masses are transported over land, with the general effect that:

1. Precipitation becomes more depleted in heavy isotopes at higher latitudes, and higher elevations (Dansgaard, 1964).

2. Precipitation inland tends to be more isotopically depleted than that falling at the coast (Dansgaard, 1964; Winnick et al., 2014).

40 3. At mid- to high latitudes precipitation isotope values vary seasonally with changing temperatures, becoming more enriched in summer and depleted in winter (Craig, 1961).

The isotope composition of precipitation at a site is also affected by the source of water vapour in air masses (Jouzel et al., 2013; Baisden et al., 2016; Crawford et al., 2013), and sub-cloud processes including re-evaporation (Risi et al., 2008; Winnick et al., 2014). Understanding of the processes controlling precipitation isotope values has led to the development of predictive

45 statistical models for global-scale mapping of precipitation isotopes values that serve also to inform on spatial patterns of surface water isotope values (Bowen and Revenaugh, 2003; Bowen et al., 2011).

A range of hydrologic processes occur at and below the land surface that alter the isotope composition of surface waters relative to the isotope composition of precipitation. These include fractionation during atmospheric exchange processes at ground,

50 water and vegetation surfaces (Evaristo et al., 2015; Ehleringer and Dawson, 1992; Gat, 1996), temporal and spatial patterns of sub-surface flow (Gonfiantini et al., 1998), and mixing between isotopically distinct waters (Klaus and Mcdonnell, 2013; Mcdonnell et al., 1991). A key limitation of current approaches to modelling stable isotope values of river water is representation of these processes across river networks (Bowen et al., 2011; Brennan et al., 2016). Geostatistical interpolation methods and linear regression used for spatial modelling of precipitation are less appropriate for surface waters because some

55 landscape characteristics that alter surface water isotope values, such as dams and lakes that increase atmospheric exchange (Gibson et al., 2016; Craig, 1961), are transferred to reaches downstream, but have no impact on nearby unconnected river networks. Hence, isotope values of surface waters are controlled by a mix of geospatial dependencies and those 'dendritic' dependencies unique to river networks (Brennan et al., 2016).

60 The water balance model approach of Bowen et al. (2011) provides a method of mapping hydrogen and oxygen isotope ratios across river networks that incorporates variation that can be modelled with interpolation approaches, and variation that follows the 'dendritic' patterns unique to river networks. This method takes advantage of spatial and seasonal predictability of precipitation isotope values, evaporative water loss and catchment discharge. Spatial patterns of residuals between predicted (modelled) and measured (annual averages of measured stream water isotope values) are then interpolated using ordinary

65 kriging to improve models of river water isotopes. Bowen et al. (2011) note that residual adjustment using ordinary kriging only indirectly considers many of the landscape attributes that may affect stream water isotope values. These attributes include

those that affect temporal and spatial patterns of sub-surface flow, such as catchment slope (Salama et al., 1993), and those that affect atmospheric exchange processes, such as the presence of dams and natural lakes (Halder et al., 2015; Gat, 1996). When spatial variability within the catchment is low and sampling density is high, ordinary kriging methods may be

70   appropriate, however, New Zealand is an example of a country with relatively large distances between long-term river monitoring sites but high variation in relief and climate over relatively short distances. Under these conditions, using regression based statistical methods with databases of explanatory environmental, rather than distance-based methods, to explain hydrological variation across the reaches of river networks provides superior prediction of spatial variability (Snelder and Biggs, 2002; Hicks et al., 2011). In this paper we follow the spatio-temporal water balance model of Bowen et al. (2011) to

75   derive of long-term water isotope values from New Zealand rivers, using precipitation isoscape coefficients of (Baisden et al., 2016), gridded meteorological data from NIWA's virtual climate station network (Tait et al., 2006; Tait, 2008), and a digital elevation map (DEM)-based river network (Snelder and Biggs, 2002). We calculate residuals between modelled surface water isotope values and values measured at 58 long-term river water sampling sites across New Zealand. We extrapolate these residuals across New Zealand using a regression method that incorporates explanatory environmental variables from the River

80   Environment Classification database (Snelder and Biggs, 2002), Freshwater Ecosystems of New Zealand (FENZ) geodatabase (Leathwick et al., 2010), as well as GIS lake data as predictors. We compare this 'regression kriging' residual estimation with ordinary kriging (Cressie, 1992; Bowen et al., 2011). We employ the method above to develop the first complete isoscape for the rivers and streams of New Zealand.

85   **2 Methods**

2.1 Water balance model for estimation of river water stable isotope values

Our initial method to calculate long-term isotope values of river water closely followed that given by Bowen et al. (2011) to calculate their 'spatiotemporally weighted water balance model' and are only briefly summarised here. For each 5 km × 5 km

90   grid cell, we estimated monthly runoff (Q) as the larger of precipitation minus evaporation (P-E), or 0.01 × P; the latter estimate (0.01 × P) provides an estimate of dry-season and dry-region runoff (Bowen et al., 2011). We estimated the annual isotopic flux of runoff from monthly-weighted values for each cell following Eq. (1):

$$\delta Q_m = \sum_{i=1}^{12}[(P_i - E_i) \times \delta_i] \qquad (1)$$

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Where δ_i is the isotope value of precipitation within the grid cell at month i. The monthly-weighted isotopic flux (δQ_m) is calculated by summing across all monthly values (i). Routing of gridded runoff started with a 30m gridded DEM of NZ. We pit-filled the grid using Spatial Analyst in ArcGIS 10.6, then calculated flow direction next for each grid cell using the d8 method (O'callaghan and Mark, 1984), which considers flow to one of 8 adjacent cells. Values of Q and δQ_m in each grid cell

100   were then accumulated downstream using the flow accumulation tool in ArcGIS.

2.2 Model input data

Gridded precipitation isotope values for New Zealand were generated using the monthly models of Baisden et al. (2016). We applied the regression coefficients of Baisden et al. (2016) to the geographical and climate predictor data given in their study,

105   including elevation, latitude, pressure, solar radiation, air temperature, vapor pressure, wind speed, soil temperature at 100 mm depth, and an estimate of potential evapotranspiration (PET). Daily climate variables, PET and precipitation were retrieved

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from the NIWA virtual climate station network (VCSN; (Tait et al., 2006; Tait and Woods, 2007)), covering the period 1997-2018. Precipitation-weighted means were produced for climate drivers and coefficients were applied to yield monthly δ^2H and δ^{18}O values for precipitation. While Baisden et al. (2016) also used VCSN interpolated data in their regressions, the VCSN

110   is regularly updated as new physical climate stations are added to or removed from the national climate network and as the spline models are periodically improved (Tait et al., 2006). Hence, we checked the results of our procedure by performing regressions between our modelled, amount-weighted monthly precipitation isotope values and measured values from the dataset of Baisden et al. (2016), comprising monthly collections from 51 sites across New Zealand between 2007 and 2009. Actual evapotranspiration (AET), as an input to the water balance model, was estimated according to the model of Porteous et

115   al. (1994) assuming a soil water storage capacity of 150 mm and a critical value of 50% of this capacity, above which AET was assumed to be equal to PET and below which PET was scaled linearly to zero. Digital elevation input data were sampled from a 30m digital elevation model of New Zealand at the respective VCSN locations. Catchment environmental characteristics were taken from the River Environmental Classification (REC; (Snelder and Biggs, 2002)) and FENZ geodatabase (Leathwick et al., 2010).

120   A summary of contributing data sources is shown in Figure 1.

2.3 Calculation and kriging of model residuals

Modelled river water isotope values were compared to annual average values from 58 sites from the New Zealand River water network (NRWQN; (Davies-Colley et al., 2011)) selected to represent catchments nationally (Yang et al., 2020). The residual

125   calculations used in this study compared predicted flow-weighted annual average values to averages of measurements. Measurements were flow-weighted monthly values at each site from April 2017-March 2020. Data from April 2017-March 2019 is published in Yang et al. (2020). For the current analysis, an additional year of data (April 2019-March 2020) was collected from all NRWQN sites following the methods of (Yang et al., 2020). Briefly, samples were taken monthly from each of the 58 sites, and river flow rates were recorded at the time when samples were collected. All samples were stored in 100 ml

130   tubes in insulated ice bins, keeping samples at approximately 0°C and in darkness in the field, and then frozen and stored at approximately -20°C in the laboratory and later thawed for analyses. Isotope analyses were conducted using an isotope ratio infrared spectroscopy (IRIS) on a wavelength-scanned, cavity ring-down spectrometer (WS-CRDS) model L1102-i (Picarro, Sunnyvale, California, USA). Any variation in isotope values resulting from diurnal patterns was minimised by collection of samples at similar times of the day. River flow rates were recorded at the time when samples were collected.

135   The locations of monitoring stations were adjusted in ArcGIS to coincide with the nearest grid cell of the stream network. Modelled isotopic compositions were extracted from each of the grid cells corresponding to a monitoring site, and the differences between modelled and observed calculated.

To improve reach-scale predictions of water stable isotope values beyond the predictions of the water balance model, we used and compared two kriging methods, Ordinary Kriging and Regression Kriging. These two methods were used to extend

140   calculated residuals between simulated and observed stable isotopes at our 58 validation sites across the New Zealand stream network. Ordinary Kriging, following the method of Bowen et al. (2011), only relies on spatial similarity (i.e. spatial autocorrelation) of the residuals. Regression kriging relies not only on spatial similarity, but also non-location predictors. In this case, the non-location predictors are catchment environmental variables available at sub-catchment scale across the New Zealand from the REC and FENZ geodatabases (Snelder and Biggs, 2002; Leathwick et al., 2010).

145   In Ordinary Kriging, the prediction is a weighted mean of the observations:

$$y_i = \sum_{k=1}^{n} \beta_k(i) y_k^o \qquad\qquad (2)$$

where y_i is the prediction at location i, y_k^o is the kth observations (k = 1, ..., n), and $\beta_k(i)$ is the kriging weight of y_k^o to y_i which is a function of locations of i and observation k and depends on the spatial autocorrelation structure of the variable (Hengl et al., 2007).

150   In Regression Kriging, the prediction is the sum of a simple regression (normally linear regression as shown below) and the result of Ordinary Kriging:

$$y_i = \sum_{j=1}^p \alpha_j x_j \ + \sum_{k=1}^n \beta_k(i) e_k^o \qquad\qquad (3)$$

where x_j is the jth environmental variable (j = 1, ..., p) and α_j is the corresponding regression coefficient, and e_k^o is the
155   residual at kth observation after the regression.

Application of regression kriging includes two steps. The first step is to apply a simple multivariable regression aiming to select the best independent non-location variables. An initial list of over 30 potential independent variables for the regression model were selected from the REC and FENZ geodatabases based on our understanding of the hydrological processes which potentially influence stream isotope components, including geological factors (e.g. slope, elevation, aspect, drainage density
160   and lake coverage), climate factors (e.g., precipitation and evaporation), and land cover (Yang et al., 2020; Yang et al., 2019). Table S1 includes descriptions of these variables; we use abbreviations hereafter as described in the table. Because many of these variables represent characteristics of the upstream catchment, they provide a representation of catchment-specific upstream processes (such as evaporation from wetlands, reservoirs, and lakes) that may affect river water isotope values. However, given the relatively small number of validation sites available (58), correlation analysis and stepwise regression
165   were applied to reduce number of independent variables. From the list of independent variables in Table S1, five were selected in the regression analysis, following the "one in ten rule" (e.g. Harrell Jr (2015)), i.e. one predictive variable can be included for every ten sites in the dataset. In the second step, spatial autocorrelation is considered together with five selected variables following Equation 3, to give the prediction.

170   The performance of ordinary kriging and regression kriging in predicting spatial patterns of residual values was assessed across the 58 long-term river monitoring sites using k-fold cross validation (Stone, 1974). In this study, we applied LOOCV and 10-fold cross-validation to assess the performance of the two kriging methods.

2.4 Data for final model validation

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Final model validation used water isotope data collated from previously published studies of rivers across New Zealand (Lachniet et al., 2021; Kerr et al., 2015; Stewart et al., 1983; Marttila et al., 2017). The literature validation dataset is provided as a supplementary file (File S1). This validation dataset contains largely synoptic sampling data; due to a paucity of annual average values in the validation dataset we included unpublished δ^2H and δ^{18}O data from 9 river sites for which
180   regional government staff have conducted monthly sampling over date ranges between 2017 and 2020. Water samples from these sites were stored and analysed following the methods of Yang et al. (2020) and annual average values were used in regression analyses. These sites are listed as *Dudley et al. unpublished data* in File S1. Because the dataset of Stewart et al. (1983) contained δ^2H but not δ^{18}O data, the δ^2H literature validation dataset is considerably larger (464 records) than that for δ^{18}O (273 records), and the δ^2H literature validation dataset also contains a higher proportion of sites in the North Island,
185   because the large dataset of Lachniet et al. (2021) is restricted to South Island rivers.

3 Results and Discussion

3.1 Precipitation isotope values

190   Our modelled estimates of long-term precipitation isotope values are a close match to those published in Baisden et al. (2016), from which we took regression coefficients; δ^2H and $\delta^{18}O$ values become increasingly enriched in northern and low elevation areas of New Zealand, with the sharpest spatial gradients at the western edges of New Zealand's central mountain ranges, which face New Zealand's prevailing West-Southwesterly winds and dominant western moisture source. Regressions between modelled, amount-weighted monthly δ^2H values and δ^2H values in monthly precipitation collections (i.e. the 2007-2010

195   monthly collection time series of Baisden et al.) resulted in $R^2 = 0.45$ and RMSE = 10.1 ‰ for monthly predictions and $R^2 = 0.79$ and RMSE = 5.1‰ for amount-weighted average values for the full 2007-2010 timespan of field sampling. Regressions between modelled, volume-weighted monthly $\delta^{18}O$ values and measured monthly precipitation $\delta^{18}O$ values resulted in $R^2 = 0.48$ and RMSE = 1.2 ‰ for monthly predictions and $R^2 = 0.80$ and RMSE = 0.55 ‰ for 2007-2010 average predictions. These fit statistics differ very slightly from those published by Baisden et al. (2016), showing improved monthly fits, but a poorer

200   longer-term fit for $\delta^{18}O$. This is likely due to updates to the climate network data used for VCSN model input, and updates to the interpolation scheme as described above.

3.2 River water stable isotopes modelled using the water balance method

Modelled, uncorrected estimates of long term river water isotope values for each of the 58 NRWQN stations ranged from -

205   68.66‰ to -32.54‰ (national average -49.83‰) for δ^2H and -9.56‰ to -5.67‰ (national average -7.56‰) for $\delta^{18}O$. Average (2017-2020) measured river water isotope values at these same NRWQN sites ranged from -77.01‰ to -19.75‰ for δ^2H (national average -46.38‰) and -10.63‰ to -2.85‰ (national average -7.25‰) for $\delta^{18}O$. The uncorrected model explained 68% of the observed variability in δ^2H values between sites, and 64% of the observed variability in $\delta^{18}O$ values between sites (Figure 2). Notably, the uncorrected model showed a tendency to under-predict both δ^2H and $\delta^{18}O$ in warmer northern and low

210   elevation sites (i.e. at the less-negative end of the range). Model under-prediction for these stations is likely due, at least in part, to evaporative enrichment of surface waters. Since these 58 NRWQN stations extend across a large latitude and elevation gradient, rivers sampled at northern and low-elevation sites flow through catchments with substantially warmer mean annual temperatures that are likely to have led to greater evaporative enrichment. Many of the sites in northern New Zealand also have large areas of lakes and wetlands in their upstream catchments (Yang et al., 2020) contributing to greater potential for

215   evaporation.

Over-prediction of both δ^2H and $\delta^{18}O$ was apparent at some sites (Figure 2). This pattern has a precedent in areas of the continental USA with high topographic relief, where the spatially-weighted model of Bowen et al. (2011), which did not consider seasonal differences in P-E, appeared to under-predict the contribution of isotopically depleted runoff from high elevations to rivers. In that study, over-prediction was ascribed to the use of a model that did not consider seasonal differences

220   in evapotranspiration; this issue was largely resolved using a temporally weighted model that considered these differences. In our study, this issue was most prominent in the South Island of New Zealand, which is characterised by high topographic relief, and high-elevation recharge sources dominate the flow of the majority of large rivers. However, in our study, we use a water balance model that considers seasonal differences in P-E but does not appear to have fully resolved this pattern. Potential reasons for this are, firstly, that the precipitation model we use over-estimates the isotope values of precipitation at high

225   elevations or in leeward, rain-shadow areas; of the eight sites where predicted $\delta^{18}O$ values exceed average measured $\delta^{18}O$ values by > 1‰, seven are in alpine-fed rivers on the leeward east of New Zealand. Kerr et al. (2015) note that small streams leeward of the Southern Alps show isotopically depleted values characteristic of spillover of orographic precipitation from the

windward west of the Southern Alps. While the linear regression approach employed in the precipitation model we used does not directly adjust for such orographic effects, it does to some extent capture areas of low δ^2H and δ^{18}O values in eastern New

230   Zealand (Baisden et al., 2016).

A second potential driver of model over-prediction of river water isotope values is surface water / groundwater interactions. Rivers in lowland, leeward New Zealand tend to gain a significant portion of their flow from groundwater (Yang et al., 2019). Where this groundwater is dominantly derived from high-elevation recharge, gaining streams and springs tend to be depleted in stable water isotopes (Stewart et al., 2018). The (uncorrected) water balance model we employ does not consider

235   groundwater pathways; this may result in error particularly in areas where gains from or losses to groundwater are considerable.

3.3 Kriging of isotope residuals

For regression kriging, simple multivariable regression applied to δ^2H residual and δ^{18}O residuals, individually, gave final lists of five independent environmental variables selected on the basis of t statistics in the two linear regressions (Table 1). These

240   variables are related to elevations (SiteElev and usCatElev), slope (usAveSlope), rainfall variability (usAnRainVar), and lake and wetland areas (usLWArea), the latter a reflection of residence time and evaporation effect. The reduced regression analyses explained over 60% of the of the uncertainty in the isotope residuals; R^2 values were 0.6 and 0.66 for the δ^2H residual and δ^{18}O residual regressions, respectively. The importance of each environmental variable (3rd column in Table 1), ranked by t statistic, shows usLWArea, usAnRainVar and usCatElev are the 3 most sensitive variables in both δ^2H and δ^{18}O residual regressions,

245   although the order of importance differs between the two analyses. Other variables in Table S1 sensitive to isotope residuals that were not included in regression included climatic variables (e.g. PET, AET, Precip, and usSolarRadSum). While including these variables could improve R^2 values for regressions (e.g. by including annual average precipitation (Precip) as a predictor, R^2 for δ^2H and δ^{18}O residuals can reach 0.76 and 0.80, respectively). However, this led to overfitting and caused the spatial isotope prediction in the following steps to be unreliable. Once the above 5 environmental predictor variables were chosen,

250   regression kriging was applied to estimate spatial patterns of residuals across New Zealand. The performance of ordinary kriging, and regression kriging were then evaluated with LOOCV and 10-Fold CV. The results of this assessment for δ^{18}O residuals are shown in Figure 3. Both LOOCV and 10-Fold CV led to similar results: regression kriging simulations are scattered around the 1:1 line while those of ordinary kriging are mostly close to a horizontal line with values around 0. There is little predictive ability for ordinary kriging, as indicated by R^2 values below 0.1 for both LOOCV and 10-Fold CV.

255   Regression kriging achieved satisfactory results, with R^2 over 0.75 for both LOOCV and 10-Fold CV. These results indicate regression kriging can be reasonably used to estimate spatial distributions of isotope residuals. It is worth noting that multiple regression contributed around 0.66 and kriging contributed around 0.1 of the total R^2. This emphasises the importance of the multiple regression step in this method, i.e. the first part of equation 3.

3.4. Spatial distributions of model residuals

260   Spatial interpolation of isotope residuals were applied to the entire national river network. Residuals interpolated using ordinary kriging (Figures 4A and 4C) show regional patterns; the water balance model tends to overpredict δ^2H and δ^{18}O values in rain-shadow areas in the east of both the North and South Islands and underpredict δ^2H and δ^{18}O values in the northern and western regions of both islands. Residuals shown in Figure 4 are calculated as the modelled minus average measured δ values for individual river reaches, so positive residuals occur where measurements were on average more depleted than the

265   model estimate. Lower isotope values in precipitation and rivers leeward of large mountain ranges are driven by fractionation during orographic precipitation processes (Stern and Blisniuk, 2002; Poage and Chamberlain, 2001), and the patterns observed across the Southern Alps indicate that the dominant source of water to rivers in leeward areas is precipitation carried over the Alps by winds (Kerr et al., 2015). The overprediction of δ^2H and δ^{18}O values (of the water balance model) in rain-shadow

areas indicates either greater recharge from high elevations to river flow within these regions, or local differences between

270 actual and predicted (modelled) precipitation isotope values. We suggest that at least some of the patterns of residuals for the water balance model (Figure 4) can be accounted as a correction of the precipitation isotope model of Baisden et al. (2016) with regard to west-to-east depletion of precipitation isotope values associated with orographic rainfall across the Southern Alps. The basis of this conclusion is shown in Figure S1, in which we have plotted residuals between measured and modelled δ^2H values for small rivers across an east to west transect through the Southern Alps (Kerr et al., 2015). The precipitation

275 isotope model (i.e. Baisden et al., 2016) appears to underpredict δ^2H values to the west of the main divide, and overpredict them to the east. The patterns seen in Figure 2 and Figure S1 indicate that these prediction errors were improved by the regression-kriging correction, though not fully resolved. Baisden et al. (2016) observe that the origins of air masses contributing to precipitation in New Zealand, and their transit across mountainous regions contribute strongly to spatial patterns of isotopes in precipitation; incorporation of this information in predictive models would seem a valuable step to improve

280 precipitation and river isotope models for New Zealand. Interpretation of spatial patterns of residuals to imply spatial patterns of hydrological processes (such as evaporation, or groundwater contributions to rivers) is dependent to some degree on the accuracy of the precipitation isotope model. Where the precipitation model does not predict regional patterns well, residuals for the river water model may reflect these errors. Spatial patterns of the strongest predictors are shown in Figure S2; we believe that relationships between residuals and some predictors may reflect issues with representation of orographic effects

285 by the precipitation model. All predictors except "usLWArea" show a strong west to east gradient; for example, areas to the east of the Southern Alps where the water balance model overpredicts river water δ^2H and $\delta^{18}O$ values have lower average catchment slopes (usAveSlp) and higher rainfall variance (usAnRainVar) than are present to the west the alps where the water balance model underpredicts river water δ^2H and $\delta^{18}O$ values. Furthermore, the significance of upstream lake and wetland area in the residuals regression can be attributed with some confidence to evaporation from surface waters with long durations of

290 exposure to the atmosphere. Wetland systems and lakes are relatively well-spread throughout New Zealand (Cromarty and Scott, 1996); glacier-carved lakes, and artificial lakes used for hydroelectric power are common through much of the Southern Alps region of the South Island, while volcanic crater lakes are present particularly in the central-eastern regions of the North Island (Figure 1G). Notably, the presence of validation sites on rivers draining major lakes creates areas of residuals that differ from regional trends. For example, within the central North Island region validation sites are sparsely spread, and roughly half

295 of the validation sites sit on major rivers draining two caldera lakes, Lake Taupo (616 km²) or Lake Tarawera (41 km²). Using ordinary kriging, these sites create an area of negative residuals (e.g. Figure 4C) that are applied as a correction to all nearby river reaches. This effect suggests that the application of distance-weighted kriging of residuals may be inappropriate for our validation dataset as discussed in section 3.3, where sites are sparse relative to both land area, patterns of lake distribution, and topographic relief. Regression kriging appeared to account to some extent for regional scale effects; regional patterns of

300 overprediction in eastern rain shadow areas are represented, as are patterns of underprediction in northern and western New Zealand. However, regression kriging does not appear to create a regional pattern of negative residuals associated with lake evaporation in the central eastern North Island (Figure 4D).

305 **3.5 Final model validation**

To further validate the results from the original water balance model (uncorrected), ordinary kriging (OK-corrected) and regression kriging (RK-corrected), we compared model results to collated literature values from previously published studies of rivers across New Zealand (Lachniet et al., 2021; Kerr et al., 2015; Stewart et al., 1983; Marttila et al., 2017), and unpublished data from 9 sites as described in section 2.4. The validation analysis required assigning a reach identification

310 number from the REC to each record reported in the citations. Using this approach, linear regression models between RK-

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corrected isotope predictions and all corresponding literature validation data explained 75.4 and 71.3%, respectively, of the δ^2H and $\delta^{18}O$ variance. The fit for δ^2H is shown in Figure 5C. Root mean squared errors (RMSE) were 6.2‰ for δ^2H on 416 degrees of freedom and 0.67‰ for $\delta^{18}O$ on 221 degrees of freedom. Datasets incorporating repeat sampling of stable isotopes in New Zealand river water are scarce; only 23 of the 418 δ^2H records in the literature validation dataset represent

315   annual averages of monthly sampling. The 186 river samples from the South Island rivers dataset of Lachniet et al. (2021) were collected within the month of November, within the austral spring snow-melt period; South Island river water isotope values at this time are generally below the annual average (Yang et al., 2020; Marttila et al., 2017). Hence, we would expect our model predictions at sites from high latitudes with snowmelt influence to be generally more isotopically enriched than our literature validation dataset. This effect appears strongest in the uncorrected model results. When smaller rivers (Strahler

320   order <3 where larger seasonal fluctuations in isotope values would be expected) were removed from the analysis, the fit of the final model improved, explaining 80.0% and 74.2%, respectively, of the δ^2H and $\delta^{18}O$ variance across the literature validation dataset, with root mean squared errors (RMSE) of 5.7‰ for δ^2H on 329 degrees of freedom and 0.62‰ for $\delta^{18}O$ on 175 degrees of freedom. The most appropriate sites for validation of our model were those 23 sites for which long-term monthly sampling records are available, enabling us to compare predicted and measured annual average values. At these

325   sites, the model explained 90.6 % of the δ^2H variance across the dataset. Root mean squared error (RMSE) was 2.99‰ for δ^2H on 21 degrees of freedom (Figure 5D).

While comparison of modelled annual average values to the full validation dataset containing predominantly single-sample values from river reaches (Figures 5A-5C) shows relatively poor model fits compared to those for long-term measurements (Figure 5D), these comparisons serve to demonstrate improvement from the uncorrected and ordinary-kriging-corrected

330   models to the final, regression-kriging corrected model. We attribute this improvement both to the representation of regional trends in residuals (such as the issue with representation of orographic rainfall effects described above), but also to improved representation of evaporation processes that can be made using a dendritic river network model (Brennan et al., 2016).

335   **3.6 Patterns and drivers of final model performance**

Patterns of precipitation isotopes, runoff and evaporation from surface water are the dominant drivers of δ^2H and $\delta^{18}O$ values in rivers

340   Across New Zealand, spatial and temporal patterns of δ^2H and $\delta^{18}O$ in precipitation and runoff are dominant drivers of δ^2H and $\delta^{18}O$ in river water (Figure 6). The (uncorrected) water balance model, which explicitly represents these factors, explained much of the variance present in our long-term river water dataset. For example, major patterns of depletion in precipitation isotopes with increasing latitude and elevation were carried through into predictions for rivers and passed downstream using the REC river network (Figures 6A and 6D). However, systematic bias was apparent; when compared to measurements from

345   river monitoring sites, the spatiotemporal water balance model showed a tendency to underpredict river water isotope values at the enriched end of the range of validation measurements and overpredict at the depleted end of this range (Figure 2).

Regression kriging residual corrections improve models of δ^2H and $\delta^{18}O$ values in rivers

350

Across the rivers of New Zealand, a water balance model corrected using regression kriging of residuals provided improved fits to measurements, compared to a model that used ordinary kriging interpolation of residuals between validation sites.

Patterns of residuals across the validation site network showed distinct patterns which we attribute to orographic rainfall effects (Kerr et al., 2015; Purdie et al., 2010), and the position of lakes and wetlands in upstream catchments (Yang et al., 2020; Halder et al., 2015). The effect of lakes and wetlands is an example of how landscape processes control δ^2H and $\delta^{18}O$ values in rivers; three factors combine to make regression kriging a particularly appropriate method to represent these processes. Firstly, lakes and rivers do not cluster predictably across New Zealand, and secondly, their effects are confined to downstream reaches. Thus, a modelling approach that considers the dendritic nature of river networks in this correction step is likely to better account for this process than one which corrects based on Euclidean distance (Brennan et al., 2016). Using a term for upstream lake and wetland areas in reach-scale regression-kriging incorporates enrichment effects of lakes and transfers this effect downstream while allowing for mixing. Thirdly, distances between validation sites in the NRWQN network are great, relative to the likely downstream extent of enrichment effects from lakes and wetlands. This raises the likelihood that corrections based on distance weighting will extend outside of the extent to where their true effect will take place. Representation of evaporation effects in the final ordinary-kriging and regression-kriging corrected models is shown using the example of the Lake Tarawera region in Figure 7. River water observed in the NRWQN validation dataset at the lake outflow is enriched in δ^2H and $\delta^{18}O$ relative to upstream precipitation and spatiotemporal model predictions, which do not account for evaporation. Using ordinary kriging, the correction factor based on the residual at the lake outflow site is applied to all nearby reaches and extends outside the catchment boundaries. Using regression kriging correction, the residual correction is passed only to downstream reaches. Both the ordinary kriging and regression kriging approaches to residual correction resulted in partial correction of bias associated with orographic rainfall effects, however spatial extents of the corrections in leeward New Zealand differ between the two kriging methods (Figure 4). This reflects the data available to predict residuals for both methods; while the ordinary kriging method in limited by the distribution of (and lack of) validation sites across high-elevation areas of southern New Zealand, using regression kriging the correction could be applied at reach scale via factors that co-vary with orographic effects (e.g. annual rainfall variance and catchment elevation, Table 1). Sharp changes in isotope values of small rivers (Kerr et al., 2015) and snowfall (Purdie et al., 2010) observed across the main divide of the Southern Alps have been associated with orographic effects. That the regression kriging correction method can apply residuals using geographical and climatological gradients that co-vary with orographic weather patterns may partly explain improved fits of this model to river water measurements nationally.

Regression kriging is vulnerable to overfitting and extrapolation

As mentioned in section 3.3, there are more than five environmental factors in the river network datasets that are spatially correlated with patterns of isotope residuals. However, it is dangerous to include all sensitive factors in regression kriging as it may cause the problem of overfitting, which is very common in regression analysis and machine learning. Machine learning methods often uses cross-validation techniques to solve the overfitting problem. In this study, there are only 58 sites which is insufficient for application of either of data-intensive machine learning methods or nonlinear regression, which increase the number of regression coefficients to fit. Instead, we focused on the five most sensitive environmental factors, following the "one in ten rule". Our results indicate this rule was appropriate for improving model performance and avoided overfitting; the addition of one more predictor in the regression model caused a wider and unreasonable range of isotope estimates in subsequent national predictions. Extrapolation was another problem we encountered in preliminary regression analysis, as the training dataset did not cover the entire range of values for all catchment characteristics. To nullify this effect, we excluded reaches from the final model where the environmental characteristics of those reaches were outside of the range of the training dataset (e.g. Strahler order 1 streams with usLWArea greater than 0.3). Solutions to overfitting and extrapolation could include adding isotope sampling sites, and increasing the range of environmental conditions across sampling sites (e.g. setting up river monitoring sites with upstream wetland areas approaching 1), or, for extrapolation, removing reaches from the final isoscape which have values for predictor variables substantially outside the range present across validation sites.

Improved understanding of patterns of precipitation isotope values can improve understanding of hydrological processes across landscapes

Spatial patterns of residuals, and predictors of residuals from the spatiotemporal water balance modelling approach could

400   potentially be applied as an investigative tool to describe flow pathways, or evaporation processes (Bowen et al., 2011). Regression kriging of these residuals allowed us to identify a suite of catchment environmental variables that were the best predictors of spatial patterns of residuals. However, as described above, patterns of residuals shown in our study are driven to some extent by systematic bias in high-elevation precipitation isotope input data. New Zealand's topographic relief creates widely divergent isotope values of precipitation isotopes depending on moisture sources (Purdie et al., 2010; Baisden et al.,

405   2016). These factors are difficult to capture with empirical models of precipitation isotopes of the kind used in this study (Bowen, 2010), however potential improvements to the precipitation isotope model could be made by incorporating high-frequency and event-based sampling, including back-trajectory calculations, and adjusting predictions based on spatial patterns of residuals (Bowen and Revenaugh, 2003; Baisden et al., 2016). Improved regional precipitation isotope models are likely to improve the performance of process-based isotope hydrology models, such as the Isotope-enabled coupled catchment–lake

410   water balance model (Belachew et al., 2016), that are designed to quantify hydrological fluxes (e.g. between rivers, lakes and groundwater) using water isotope data.

4. Final conclusions and implications

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We have successfully produced isoscapes of δ^2H and $\delta^{18}O$ for the river network of New Zealand by employing a water balance-based model, enhanced by a regression kriging method to capture catchment characteristics not accounted for by the simple water balance. Although the final model performs well, future research is needed to improve model input data and identify the processes underlying spatial patterns of residuals identified by regression kriging. Further inclusion of these processes which

420   contribute to fractionation and source mixing will reduce the need for correction methods, which are descriptive of current patterns, but may not have predictive value with changing climate and hydrological modification.

Our results have important implications for studies of providence and migration that employ these stable isotopes as tracers, as spatial patterns of δ^2H and $\delta^{18}O$ in river waters across New Zealand show distinct differences from patterns of precipitation. Differences between precipitation and river water isotope values are particularly evident across elevation gradients; New

425   Zealand's high central mountain ranges create strong elevation gradients in precipitation isotopes, and lowland regions receiving more isotopically enriched rainfall are intersected by alpine-fed rivers bearing isotopically depleted water. Understanding how isotopic values vary in water sources for biota across elevation gradients may be of particular benefit to those studies that attempt to attribute organic material (such as sediment-bound organic material transported in rivers) to particular elevation bands (Upadhayay et al., 2017; Feakins et al., 2016). Development of reach-specific predictions for water

430   stable isotopes may also benefit ecological studies that examine movement of aquatic organisms (e.g. Brennan et al. (2015)); fine-scale study of animal movements across river networks can benefit from maps of river water isotope variation across similarly fine spatial scales.

435   **Code and data availability**

Modelled river water isotope values generated as described in this paper are available for download via NIWA's *NZ River Maps* site at https://shiny.niwa.co.nz/nzrivermaps/

River water measurements for model correction can be downloaded from the Global Network of Isotopes in Rivers (GNIR) database of the International Atomic Energy Agency (IAEA) through the WISER portal (Water Isotope System for Data

440 Analysis, Visualization and Electronic Retrieval).

A compiled literature validation data file used to produce Figure 6 is provided as supplementary file S1.

Environmental predictor datasets and code used in this work are available on request from the authors.

Author Contributions

BDD, JY and US contributed to project conceptualization, methodology, investigation, data curation and formal analysis.

445 BDD, JY and US contributed to writing and editing of the original draft. SG contributed to methodology, formal analysis, data curation and editing of the original draft. BDD led project administration.

Competing interests

No competing interests

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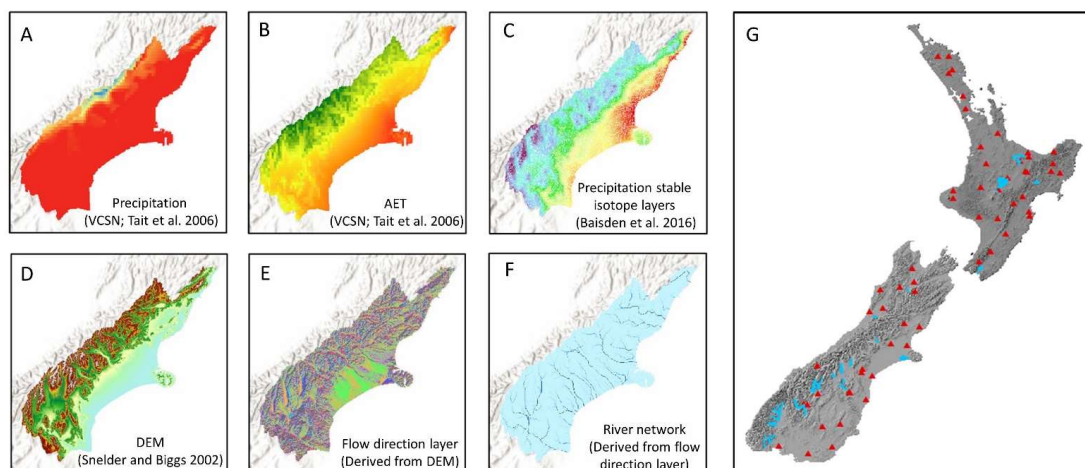
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Figures

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Figure 1. GIS layers and data sources used in model development. Panels A-F show GIS layers used for water balance modelling, plotted over the Canterbury region in New Zealand's South Island. Precipitation, Actual Evapotranspiration (AET), and stable isotope values of precipitation (panels A-C) are used to calculate catchment-scale flow-weighted isotope values of

575 recharge (δQ, i.e. flow * isotope δ value)). The river network (F) is derived from the DEM (D) and flow direction (E) layers by setting a suitable flow accumulation threshold. Catchment δQ values are routed downstream through the river network to generate reach-scale estimates of δ^2H and $\delta^{18}O$. Panel G shows river water isotope measurement sites (triangle) used for model correction, and major lakes (blue area).
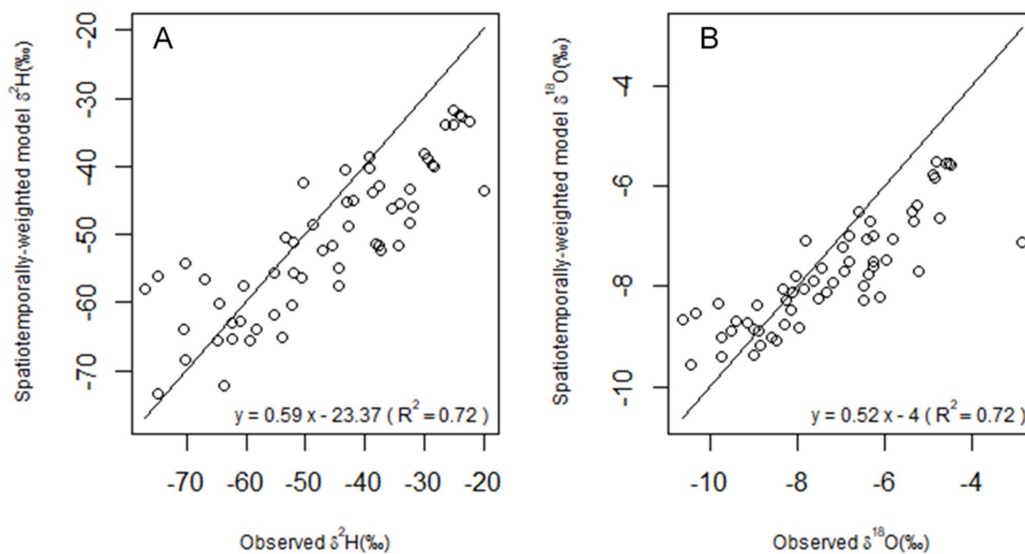
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Figure 2. Relationship between modelled and observed δ^2H (Panel A) and $\delta^{18}O$ (Panel B) at 58 long-term river water monitoring sites across New Zealand. Modelled isotopes were the long-term averages of simulated isotopes computed following the water balance model approach of Bowen et al. (2011). The solid line shows a 1:1 fit. The modelled tends to over-predict river water isotope at the more-negative end of the range (e.g. at high-latitude cooler southern sites) and under-predict at the less-negative end of the range (e.g. warmer, northern sites).
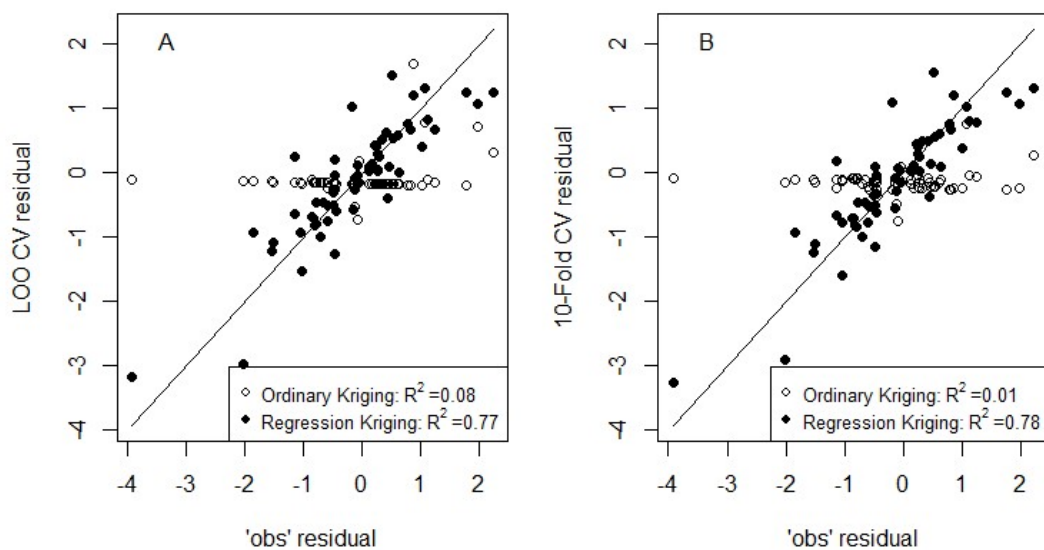
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Figure 3. Comparison between observed residuals and spatial predictions of residuals made using two interpolation methods
– Ordinary Kriging and Regression Kriging. Observed residuals are differences between spatiotemporal model predictions of
$\delta^{18}O$, and measurements from 58 long term river monitoring sites across New Zealand. Comparison with estimates of residuals
generated using Leave-One-Out Cross-Validation (A) and 10-fold cross validation (B) suggests improved fit of regression
595   kriging, relative to ordinary kriging.
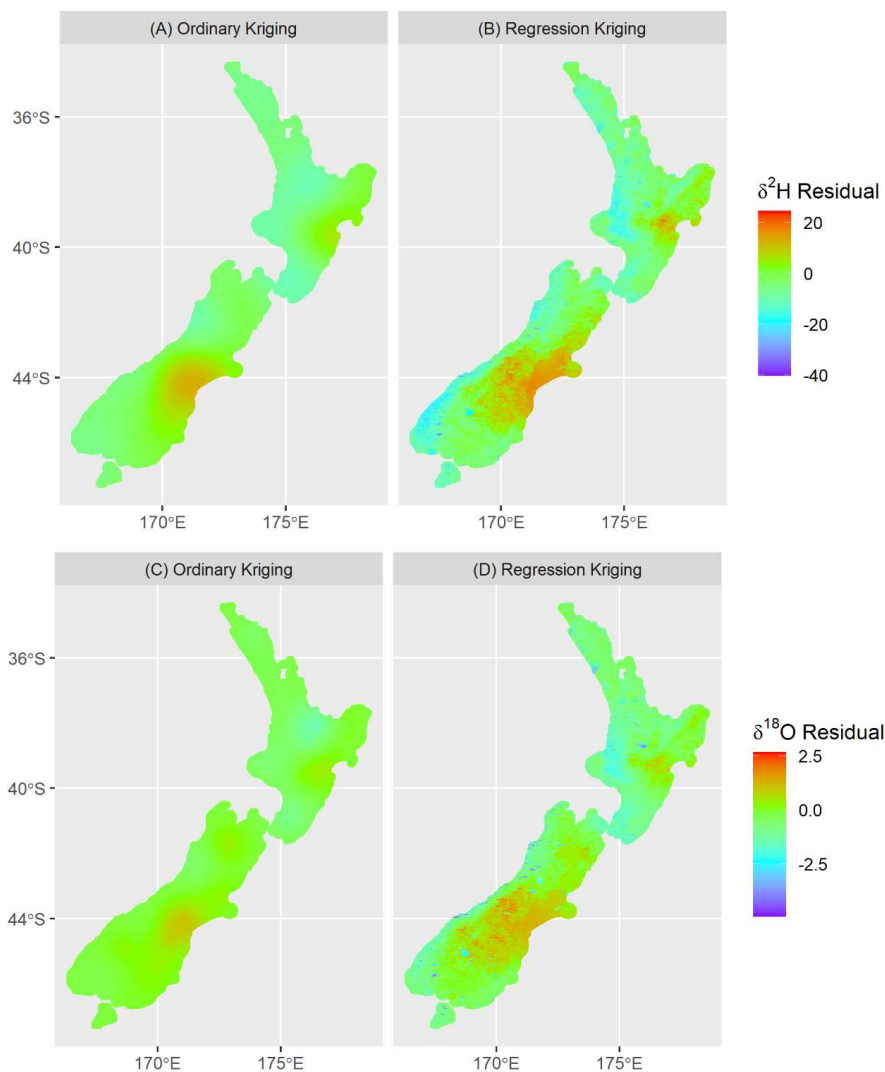
Figure 4. Distribution of isotope residuals (i.e. difference between modelled and observed isotopes) from ordinary Kriging (A and C), and regression Kriging (B and D). Positive values equate to a negative adjustment of river δ^2H and δ^{18}O values from the water balance model, as seen in leeward (eastern) areas of both the North and South Island. Ordinary kriging results in regional zones of negative isotope residuals around validation sites downstream from lakes and wetlands (such as in the central North Island), while regression kriging predicts negative isotope residuals in low-elevation western areas, as well as in all lakes and wetlands and their downstream reaches.
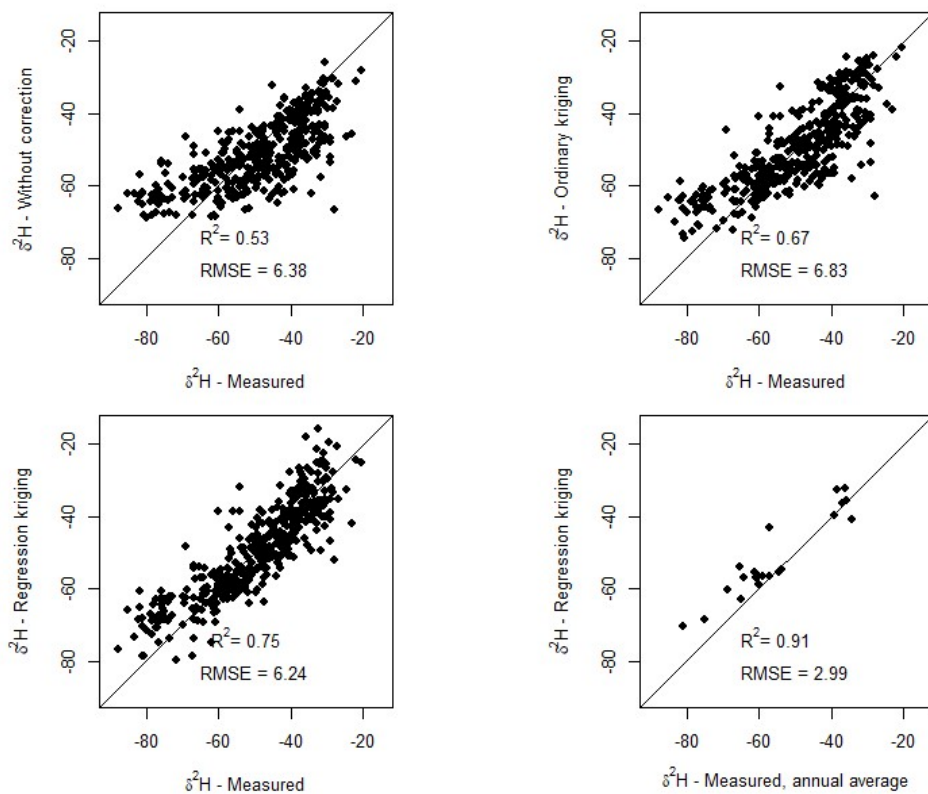
Figure 5. Comparison of literature values of water δ^2H across New Zealand rivers with predicted long-term average δ^2H values
610   from: the uncorrected water balance model (A); ordinary kriging corrected model (B); and regression kriging corrected model
(C). Panel D shows a comparison between predictions of the regression kriging corrected model with mean annual measured
values at sites with > 1 year of monthly data. Lines show a 1:1 relationship.

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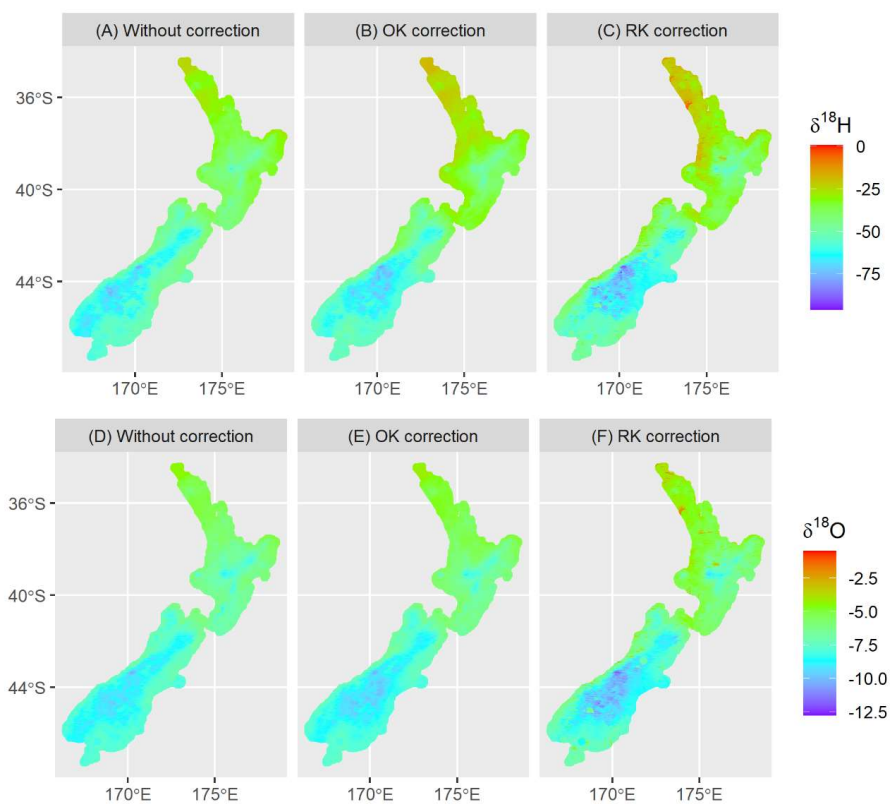
620   Figure 6. Predicted δ^2H and $\delta^{18}O$ of surface water of New Zealand. Panels A and D show uncorrected values from the water

balance model. Panels B and E gives residual-corrected values based on ordinary Kriging (OK correction). Panel C and F gives

residual-corrected values based on regression Kriging (RK correction).
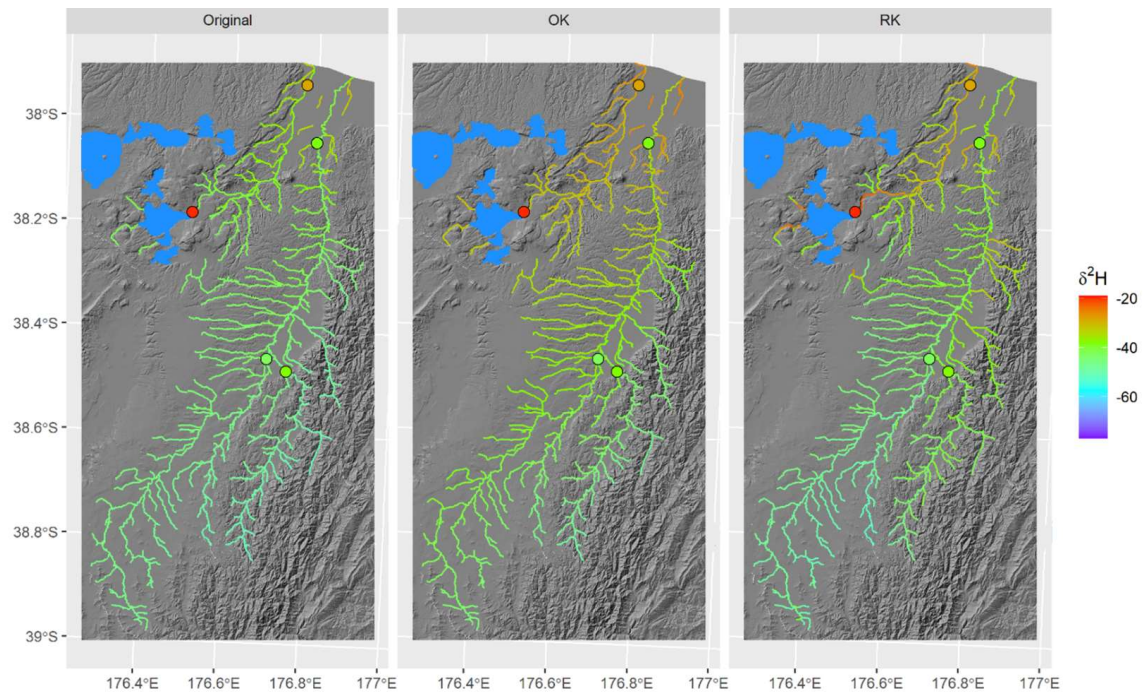
625 Figure 7. Comparison of modelled δ2H values of river water across two neighbouring North Island basins (Tarawera basin

and Rangitaiki basin). Higher δ2H values from 2H-enriched precipitation lower in these catchments are represented by the

water balance model ('Original' panel A). Residual correction using ordinary kriging (OK) extends the enrichment effect of

Lake Tarawera (top left of each panel) across the entire region. Using regression kriging (RK), the lake enrichment is mostly

confined to downstream reaches. Points denote the locations and observed δ2H values at the gauging sites.

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Tables

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Table 1. Selected environmental variables and related information, and importance ranks in the regression for δ^2H and δ^{18}O residuals

Variable Name	Importance rank for δ^2H residual	Importance rank for δ^{18}O residual	Description	Units	Source
SiteElev	5	5	Elevation of the sampling site (or locations for prediction)	m	FENZ (Leathwick et al. 2010)
usCatElev	2	2	Mean elevation of the upstream catchment	m	REC (Snelder and Biggs, 2002)
usAveSlope	4	4	Mean slope of upsteram catchment	ºC	REC (Snelder and Biggs, 2002)
usAnRainVar	1	1	Coefficient of variation of annual catchment rainfall	mm	FENZ (Leathwick et al. 2010)
usLWArea	3	3	Percentage of catchment with lakes, and inland and coastal wetlands	-	FENZ (Leathwick et al. 2010)

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